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## NO DRAWINGS

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(54) STYRENE POLYMER MATERIALS HAVING  
 FLAME-RESISTANT PROPERTIES

(71) We, CHEMISCHE WERKE HÜLS AKTIENGESSELLSCHAFT, a German Company, of 4370 Marl, Germany, do hereby declare the invention, for which we pray that a Patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following Statement:—

Mouldings of styrene polymers which are self-extinguishing or which cease to burn outside an igniting flame are required for many applications in the building field or particularly in the electrical industry.

Self-extinguishing moulding materials can be obtained by various methods (Vogel, Flammfestmachen von Kunststoffen (1966)).

Thus it is known that substances containing chlorine may be used as fire retardants for thermoplastics. To achieve an adequate flame retarding effect it is necessary to add large amounts of the substances containing chlorine. Certain properties are however detrimentally affected thereby. Moreover discolouration and decomposition are observed in processing.

It is also known that organic compounds containing bromine are effective in smaller amounts and that their effectiveness can be further increased by adding a great variety of activators. These are usually aliphatic and particularly cycloaliphatic bromine compounds. These compounds are particularly favourable in flameproof finishing of expanded plastics of polystyrene. These compounds are however not very suitable for finishing conventional compact mouldings because of their too low resistant to heat.

Organic bromine compounds having aromatically combined bromine have also been used for flameproof finishing of polyolefines. These compounds are unsuitable however for flameproofing compact polystyrene mouldings because of their low effectiveness.

Bromination products of alkylbenzenes having a total of eight to ten carbon atoms in which at least on one alkyl group two hydrogen atoms have been replaced by bromine have already been described as flame retardants (Canadian Patent Specification No. 558,230). Similarly to benzyl bromide or xylylene dibromide, these compounds exhibit however a low chemical and thermal resistance. In particular however they are hazardous physiologically because when they are used there is a risk of irritation of the mucuous membrane.

In accordance with the invention, there are provided flame-resistant thermoplastic compositions of styrene polymers as hereinafter defined and organic bromine compounds with or without organic chlorine compounds and/or antimony trioxide and with or without expanding agents, which contain as the organic bromine compound a bromination product of hexamethylbenzene in an amount of from 1 to 20% by weight, preferably from 1 to 10% by weight, with reference to the styrene polymer.

By "styrene polymers" we mean homopolymers of styrene and  $\alpha$ -methyl-styrene, and copolymers (which term includes graft polymers) of styrene and/or  $\alpha$ -methyl-styrene, which copolymers contain at least 50% by weight of polymerised units selected from styrene and  $\alpha$ -methyl-styrene units, and mixtures (blends) of such polymers with elastomeric polymers which contain no styrene or  $\alpha$ -methyl-styrene or less than 50% by weight of these monomers. Co-monomers that are suitable as the "other comonomers" are acrylonitrile, esters of acrylic acid, esters of methacrylic acid and elastomer-forming monomers.

By elastomer-forming monomers we means monomers or monomer mixtures which polymerise to form elastomers or which copoly-

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merise with any of the above-listed monomers and/or comonomers to form elastomers.

Impact-resistant styrene polymers, which contain elastomeric constituents, and polymers known as ABS-polymers, may also be used. The impact-resistant styrene polymers may be obtained by mixing styrene polymers with elastomeric constituents or by grafting styrene, with or without polymerisable monomers, onto the elastomeric components.

Naturally mixtures of these impact-resistant styrene polymers may also be used.

The production of the hexamethylbenzene (for which no claim is made within the scope of the present application) may be carried out for example by trimerisation of butyne-(2), for example by the process according to German Patent 1,280,827.

Bromination of hexamethylbenzene may also be carried out by known methods, for example by allowing bromine to act on hexamethylbenzene at elevated temperatures in a suitable solvent. Thus for example single bromination components may be used, as for example hexa - (bromoethyl) - benzene, penta - (bromomethyl)methylbenzene, tetra - (bromomethyl)-dimethylbenzene or bromomethylpentamethylbenzene. The mixture of the various stages of bromination obtained in the bromination are also suitable. Accordingly brominated hexamethylbenzenes whose mean bromine content is from one to six bromomethyl groups (equivalent to from 33 to 76% by weight of bromine) advantageously those containing an average of from 2 to 5.5 bromomethyl groups (equivalent to from 50 to 74% by weight of bromine) may be used.

The brominated hexamethylbenzenes are used in an amount of from 1 to 20% by weight, advantageously from 1 to 10% by weight, with reference to the styrene polymer, the brominated hexamethylbenzenes or mixtures thereof preferably being used in such an amount that the moulding material contains at least 0.5% by weight of bromine.

Chlorine compounds and/or antimony compounds may be used in addition to the brominated hexamethylbenzenes.

In any case it is advantageous to use chlorine compounds having a high chlorine content in order to keep the amount thereof in the plastics material as low as possible. Examples of suitable chlorine compounds are chloroparaffins or chlorinated polyethylenes. The proportion of antimony compounds such as antimony trioxide should obviously be kept as low as possible. Generally amounts of from 1 to 5% by weight with reference to the styrene polymer are adequate.

The moulding materials may contain conventional additives such as stabilisers, lubricants, fillers, dyes or plasticisers, as well as the flame retardants.

The moulding materials finished with the flame retardants according to this invention are preferably used for the production of compact mouldings because the advantages of the additives according to this invention are then used to best effect on account of their chemical and thermal stability. They may however also be used for the production of expanded mouldings.

The brominated hexamethylbenzenes, with or without the organic chlorine compounds and/or antimony trioxide, may be mixed together on in sequence with the styrene polymer and any other conventional additives, for the production of the moulding material. For example they may be introduced into the plastics on rollers, in an extruder or in a kneader. It is also possible to add bromine compounds according to this invention before, during or immediately after the polymerisation.

The self-extinguishing property of the moulding material is tested in the following way: a moulding having the dimensions 100 mm x 2 mm is used for the test. The test sample is suspended vertically and a slightly illuminated bunsen burner flame (length of the flame about 2 cm) is held at the lower edge until it begins to burn; the afterburning time after the flame has been withdrawn is determined in each case. Ignition is carried out a total of five times with each sample.

In some cases the burning behaviour is also determined by the method according to ASTM D 636—56 T. In this a test sample 127 mm x 12.7 mm x 3 mm is clamped horizontally twisted through 45° on the horizontal axis. The flame of a bunsen burner (diameter about 5mm; height of flame about 12 to 13 mm) is applied so that the tip of the flame reaches the end of the test sample; exposure to the flame 2 x 30 seconds. If the sample does not burn any further at all, the classification is "non-burning by this test". If the material burns afterwards but without exceeding the 4-inch mark, the material is classified as "self-extinguishing by this test". If the material burns further still, it has the classification "burning by this test".

The bromination products of hexamethylbenzene used according to the invention are completely resistant to hydrolysis under storage and processing conditions, in contrast to known bromoalkyl compounds of incompletely substituted benzene. They are odourless and not irritating to the skin.

Brominated hexamethylbenzenes used according to the invention has higher thermal stability with simultaneous high effectiveness than purely aliphatic bromine compounds. Owing to this outstanding thermal stability, neither discolouration nor corrosion phenomena occur at high processing temperatures.

The invention is illustrated by the following Examples.

#### EXAMPLE 1

100 parts by weight of an impact-resistant polystyrene which contains as a rubber constituent, 9% by weight of a copolymer of butadiene with a minor proportion of styrene, 8 parts by weight of a bromination product of hexamethylbenzene containing per molecule an average of 5.5 bromine atoms, 2 parts by weight of a waxy chloroparaffin (70% of chlorine) and 2 parts by weight of antimony trioxide and also 0.5 part by weight of a lead phosphite are intimately mixed and homogenised in an extruder. The pale granules obtained are pressed into boards from which test specimens required for a fire test are cut. Afterburning times of 8, 7, 9, 6 and 5 seconds are determined. According to ASTM D 635—56 T, the product obtained has in each case the evaluation "non-burning" when test specimens having a thickness of 2 mm and 4 mm are tested.

#### EXAMPLE 2

As described in Example 1, 8 parts by weight of hexa(bromomethyl)-benzene and 5 parts by weight of antimony trioxide are incorporated into an impact-resistant polystyrene which contains 5.5% by weight of an elastomeric copolymer of butadiene with a minor proportion of styrene. The afterburning time in the fire test is 3, 2, 3, 6 and 7 seconds.

If 10 parts by weight of hexabromodiphenyl ether is used instead of 8 parts of hexa-(bromomethyl)-benzene, the test specimen burns away completely in the course of about 100 seconds after being ignited once or twice.

If 10 parts by weight of a cyclic organic chlorine compound, having a chlorine content of about 65%, and 10 parts by weight of antimony trioxide are mixed with the impact-resistant polystyrene instead of 8 parts by weight of hexa-(bromomethyl)-benzene and homogenised on rollers, the test specimen burns away after a single ignition.

#### EXAMPLES 3 to 7

100 parts by weight of an impact-resistant polystyrene which contains 5.5% by weight of an elastomeric copolymer of butadiene with a minor proportion of styrene is mixed with 2 parts by weight of  $Sb_2O_3$  and 2 parts by weight of a waxy chlorinated paraffin having a chlorine content of 70% and in each case 6 parts by weight of a bromination product of hexamethylbenzene as set out in Table 1 and homogenised on the rollers. In the Table 1 the following abbreviations are used:

Ex = Example No.

NoBr = average number of bromine atoms per molecule

BrA = bromine content of the additive in %

BrM = bromine content of the mixture in %

ABT = afterburning time in seconds:

TABLE 1

Ex	NoBr	BrA	BrM	ABT
3	6	76	4.1	7,9,6,5,8
4	5.5	74	4.0	7,4,6,3,4
5	5	72	3.9	7,5,6,4,8
6	4	67	3.7	10,5,11,10,8
7	3	60	3.3	5,3,8,6,12

#### EXAMPLES 8 to 12

100 parts by weight of each of the types of polystyrene set out in Table 2 is mixed with 8 parts by weight of hexa-(bromomethyl)-benzene, 2 parts by weight of anti-

mony trioxide and 2 parts by weight of a waxy chlorinated paraffin having a chlorine content of 70%; the mixtures are homogenised on a roller and then comminuted. Press-moulded boards are prepared from the

broken granules and test strips are made from the boards. The bromine content of the mix-

tures in each case is 5.4% and the chlorine content is 1.3%.

TABLE 2

Ex	Type of polystyrene	Afterburning time in seconds
8	impact resistant polystyrene (blend of polystyrene with 7.5% of polybutadiene rubber)	11,14,12,14,17
9	impact-resistant polystyrene (blend of polystyrene with 9% by weight of a butadiene-styrene rubber in which butadiene is the predominant monomer)	4,5,14,12,8
10	impact resistant polystyrene (blend of polystyrene with 3.5% by weight of a styrene-butadiene rubber in which butadiene is the predominant monomer)	3,2,4,5,7
11	styrene homopolymer K value 58	4,3,4,8,8
72	styrene homopolymer K value 69	3,5,6,1,2

## EXAMPLE 13

100 parts by weight of a polystyrene (homopolymer) having a K value of 63 is mixed with 4 parts by weight of a bromination product of hexamethylbenzene containing 5.5 bromine atoms per molecule and homogenised on rollers. The afterburning times of the test strips are 1—0—2—1—1 seconds.

## EXAMPLE 14

100 parts by weight of a copolymer of styrene 77% and acrylonitrile 23% having a K value of 63 is mixed with 2 parts by weight of a bromination product of hexamethylbenzene containing 5.5 bromine atoms per molecule and homogenised on rollers. The afterburning time of the test strips are 0—0—0—0—0 second.

The K values are determined according to the method of H. Fikentscher, *Cellulose-chemie*, 13 (1932), page 60.

## WHAT WE CLAIM IS:—

1. A flame-resistant thermoplastic composition comprising a styrene polymer as hereinbefore defined and from 1 to 20% by weight (with reference to the styrene polymer) of a bromination product of hexamethylbenzene.

2. A flame-resistant thermoplastic composition as claimed in claim 1 in which the content of bromine in the form of bromination

products of hexamethylbenzene is at least 0.5% by weight.

3. A flame-resistant thermoplastic composition as claimed in claim 2 which contains 1 to 10% by weight (with reference to the styrene polymer) of the bromination product.

4. A flame-resistant thermoplastic composition as claimed in claim 1, 2 or 3 which also contains a chlorine compound.

5. A flame-resistant thermoplastic composition as claimed in any of claims 1 to 4 which contains antimony trioxide.

6. A flame-resistant thermoplastic composition as claimed in any of claims 1 to 5 which also contain an expanding agent.

7. A flame-resistant thermoplastic composition as claimed in any of claims 1 to 6 wherein the styrene polymer is a homopolymer of unsubstituted styrene.

8. A flame-resistant thermoplastic composition as claimed in any of claims 1 to 6, wherein the styrene polymer is a copolymer containing at least 50% of polymerised units of styrene or  $\alpha$ -methylstyrene.

9. A flame-resistant thermoplastic composition as claimed in any of claims 1 to 6 wherein the styrene polymer is a homopolymer of  $\alpha$ -methylstyrene.

10. A flame-resistant thermoplastic composition as claimed in any of claims 1 to 6, wherein the styrene polymer is a blend of a

homopolymer of unsubstituted styrene with a minor proportion of an elastomer.

11. A flame-resistant thermoplastic composition as claimed in any of claims 1 to 10
- 5 substantially as described in any of the foregoing Examples.

12. A flame-resistant moulded article when

made from a thermoplastic composition as claimed in any preceding claim.

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